EFFECTS OF SPECIES, SPECIMEN SIZE, AND HEATING RATE ON CHAR YIELD AND FUEL PROPERTIES[1]

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ABSTRACT

Char yields from red maple, white oak, longleaf pine, and hybrid poplar (NE 388) wood specimens of four different particle sizes carbonized in a flowing nitrogen atmosphere with heating rates of 5, 15, and 25 C/min up to 250 C, 400 C, and 600 C were examined. Although species, particle size, and heating rate trends were evident, regression analysis showed final carbonization temperature to be the most important factor influencing char yield.

Carbonized and noncarbonized specimens were subjected to elemental analysis and gross heat of combustion determinations. Regression analysis established a significant relationship of carbon and hydrogen content with final carbonization temperature. A linear relationship was found between gross heat of combustion values and carbon contents of wood and char specimens. An equation to theoretically calculate gross heat of combustion values of wood and char was developed through modification of Dulong's formula.

Keywords: Pyrolysis, char, gross heat of combustion.

INTRODUCTION

Pyrolysis is the thermal degradation of organic material heated in an inert or oxygen-deficient atmosphere and is an important stage in the course of all gasification and combustion reactions (Reed and Jantzen 1979). Previous research has focused on either fast (flash) pyrolysis, which favors the formation of volatile products (Milne 1979; Shafizadeh 1968; Lewellen et al. 1976), or slow pyrolysis, which favors the formation of char (Slocum et al. 1978; McGinnes et al. 1971; Beall et al. 1974; Hammond et al. 1974; Shafizadeh 1968; Kanury 1972).

The formation of volatile products and char during pyrolysis has been investigated using different thermal analysis techniques. Thermogravimetric analyses have shown that hemicelluloses and cellulose decompose to form mostly volatile products, while lignin, due to its relatively high thermal stability, contributes the most to the charred residue when pyrolysis temperature exceeds 350 C (Beall 1969; Roberts 1970; Milne 1979; Cheremisinoff and Morresi 1976; Shafizadeh 1980).

Char produced during pyrolysis has many potential uses. As a result char properties such as mass loss, dimensional shrinkage, density, and ultrastructure have been analyzed and reported (Beall et al. 1974; Slocum et al. 1978; Susott 1980; Moore et al. 1974; Baileys et al. 1982; McGinnes et al. 1971; Blankenhorn et al.

1972, 1978). Fuel properties of the char have also been determined, and the higher heating values (gross heat of combustion) for char, condensate, and noncondensible gas have been reported (Knight and Bowen 1975; Baileys and Blankenhorn 1982; Susott et al. 1975; Demeter et al. 1977). In order to predict fuel properties, Susott et al. (1975) have demonstrated that a linear relationship exists between gross heat of combustion and carbon content of char. All of these properties are needed for determining the usefulness of char produced during pyrolysis.

The purposes of this research were to: 1) determine the effect of species, particle size, heating rate, and carbonization temperature on char yield from wood carbonized in a flowing nitrogen atmosphere; and 2) develop an equation to calculate gross heat of combustion of wood and char through modification of Dulong's formula (Babcock and Wilcox 1975). The experimental procedure was designed to characterize noncarbonized (control) and carbonized (char) specimens, determine gross heat of combustion values for all specimens and determine elemental composition for selected specimens. These data were used to determine the effects of the selected parameters on char yield and develop an equation to calculate gross heat of combustion for char.

MATERIALS AND METHODS

Pyrolysis

Four species (Fig. 1) were chosen for carbonization: red maple (*Acer rubrum* L.), a relatively low specific gravity hardwood; white oak (*Quercus alba* L.), a relatively high specific gravity hardwood; hybrid poplar (*Populus maximowiczii* × *trichocarpa* NE 388), an intensive culture species; and longleaf pine (*Pinus palustris* Mill.), a softwood. Specimens were machined into four sizes with the following surface area to volume ratios: 8 (1.91 cm cubes), 12 (1.27 cm cubes), 51 (0.32 × 0.32 × 0.25 cm rectangles), and 100 (wood milled to pass a 40-mesh screen with a 425-micron opening). Three oven-dry specimens of each species/size combination were pyrolyzed in a flowing nitrogen atmosphere (270 cc/min) at three different heating rates (approximately 5, 15, and 25 C/min) up to three different maximum temperatures (about 250 C, 400 C, and 600 C). This permitted comparison of results with the results from other thermal analyses of wood (Kanury 1972; Beall et al. 1974; Moore et al. 1974; Baileys and Blankenhorn 1982; Blankenhorn et al. 1978).

Oven-dry mass of the wood specimens was recorded prior to carbonization. The specimens were placed in a ceramic tube and heated in a flowing nitrogen atmosphere. Electric furnace temperature was controlled to achieve the desired heating rates and pyrolysis temperatures. A chromel alumel thermocouple was placed in the gas stream near the center of the three specimens and was connected to a digital temperature readout in order to record pyrolysis temperature. The time and temperature at the start and finish of each pyrolysis test were recorded.

After the desired final pyrolysis temperature was reached, the specimens remained in the furnace in a flowing nitrogen atmosphere until the furnace temperature dropped to 105 C. The specimen residence times during the cooling process for all specimen sizes lasted approximately 1 h, 1½ h, and 3 h for maximum temperatures of 250 C, 400 C, and 600 C, respectively. The cooled specimens were removed from the pyrolysis apparatus and placed in a desiccator, and their mass was recorded after reaching ambient temperature (Lunden 1982).
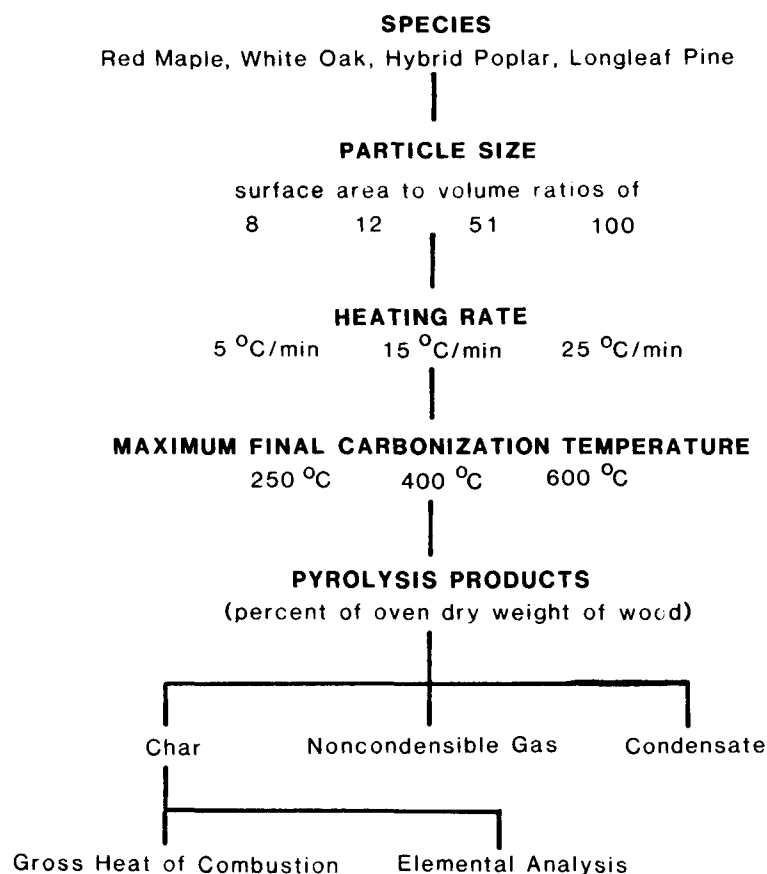
SPECIES

Red Maple, White Oak, Hybrid Poplar, Longleaf Pine

PARTICLE SIZE

surface area to volume ratios of

8   12   51   100

HEATING RATE

5 °C/min   15 °C/min   25 °C/min

MAXIMUM FINAL CARBONIZATION TEMPERATURE

250 °C   400 °C   600 °C

PYROLYSIS PRODUCTS

(percent of oven dry weight of wood)

Char   Noncondensible Gas   Condensate

Gross Heat of Combustion   Elemental Analysis

FIG. 1. Experimental design for determining the effects of species, particle size, heating rate and temperature on char properties.

Elemental analysis

The Carlo Erba Model 1106 Elemental Analyzer was used to determine nitrogen, carbon, and hydrogen content of a representative sampling of carbonized specimens and all control (noncarbonized) specimens as a percentage of oven-dry weight. Specimens were milled (pass a 60-mesh screen with a 250 micron opening), oven-dried, and stored in a $CaSO_4$ filled desiccator to prevent moisture sorption prior to testing.

Gross heat of combustion

Gross heat of combustion values of control and carbonized specimens were determined in an adiabatic calorimeter in accordance with ASTM D 2015. All specimens were oven-dried prior to testing.

Statistical analysis

Stepwise regression was used to determine the relationship between char and species, particle size, heating rate, final carbonization temperature, and all possible interactions (size × rate, size × temp, rate × temp, size × rate × temp). This

TABLE 1.   *Average char yield (percent of oven-dry weight) as a function of final carbonization temperature.*

Surface area to volume ratio	Heating rate (C/min)	Char yield (percent oven-dry weight)					
		Final carbonization temperature (C)			Final carbonization temperature (C)		
		250	400	600	250	400	600
		Red maple			*White oak*		
100	5	97.28	27.53	19.99	94.25	34.13	25.39
	15	95.57	28.21	21.20	94.95	34.15	25.72
	25	97.02	25.86	20.32	94.97	32.37	24.46
51	5	94.68	28.03	22.21	97.22	32.51	25.80
	15	98.24	26.37	22.12	94.58	31.10	25.14
	25	98.24	25.29	21.71	98.89	25.76	24.17
12	5	96.18	30.49	23.44	95.84	38.42	29.07
	15	96.86	28.31	23.03	94.46	35.97	27.29
	25	96.59	25.80	21.36	95.85	32.13	25.53
8	5	98.60	31.08	25.32	94.08	38.87	28.23
	15	97.76	28.52	22.72	95.25	36.63	26.88
	25	99.16	31.78	22.21	93.55	34.06	25.45
		Longleaf pine			*Hybrid poplar*		
100	5	98.06	31.34	23.59	96.02	27.03	21.72
	15	96.00	32.60	23.36	95.21	28.04	21.40
	25	95.79	30.32	22.41	94.06	26.21	20.85
51	5	97.32	31.17	23.40	99.08	26.54	22.81
	15	95.19	30.09	22.79	94.84	24.45	21.40
	25	99.23	29.99	22.63	96.64	25.32	21.03
12	5	96.54	35.08	25.56	96.31	30.60	23.68
	15	97.17	33.14	24.64	91.91	30.06	24.75
	25	97.64	32.65	22.78	95.42	29.76	21.79
8	5	97.65	34.90	25.71	96.09	30.84	24.10
	15	97.61	32.50	24.10	98.30	28.29	24.02
	25	97.55	33.02	23.28	96.45	26.68	22.65

procedure performed a regression analysis in a stepwise manner of all possible models and the best one-variable model, two-variable model, etc. were determined on the basis of the maximum coefficient of determination (R^2) value. All regression relationships were significant at the 0.05 level. Analysis of variance methods were used to determine statistically significant (at the 0.05 level) differences among char yields, carbon and hydrogen contents and gross heat of combustion values.

RESULTS AND DISCUSSION

Pyrolytic product yield

An average value for all species, sizes, and heating rates indicated that about 96%, 31%, and 24% of the original oven-dry weight of wood remained after carbonization to 250 C, 400 C, and 600 C, respectively (Table 1). A small mass loss of the wood occurred at temperatures up to 250 C, while a substantial mass loss occurred at temperatures between 250 C and 400 C. An additional small amount of mass was lost at temperatures between 400 C and 600 C. These results were similar to previously published data (Kanury 1972; Beall et al. 1974; Moore

TABLE 2. *Summary of regression equations.*

Species	Regression relationship (0.05 significance level)	Coefficient of determination (R^2)
	Char yield and final carbonization temperature[1]	
Red maple	Char yield = 135 − 0.20T	0.75
White oak	Char yield = 131 − 0.19T	0.76
Longleaf pine	Char yield = 136 − 0.20T	0.76
Hybrid poplar	Char yield = 133 − 0.20T	0.73
	Carbon content and final carbonization temperature[1]	
Red maple	C = 33 + 0.09T	0.89
White oak	C = 35 + 0.09T	0.82
Longleaf pine	C = 36 + 0.09T	0.86
Hybrid poplar	C = 34 + 0.09T	0.88
	Hydrogen content and final carbonization temperature[1]	
Red maple	H_2 = 7.36 − 0.01T	0.89
White oak	H_2 = 7.08 − 0.01T	0.80
Longleaf pine	H_2 = 7.61 − 0.01T	0.90
Hybrid poplar	H_2 = 7.39 − 0.01T	0.89
	Gross heat of combustion and carbon content[2]	
Red maple	Hg = 643 + 84C	0.98
White oak	Hg = 767 + 81C	0.99
Longleaf pine	Hg = 820 + 82C	0.99
Hybrid poplar	Hg = 671 + 83C	0.99

[1] Char yield, carbon content, and hydrogen content values are in percent of oven-dry weight and final carbonization temperature (T) is in C.
[2] Gross heat of combustion values are in cal/g and carbon content values are in percent of oven-dry weight.

et al. 1974; Baileys and Blankenhorn 1982; Blankenhorn et al. 1978), and correspond with known thermal degradation patterns of cellulose, hemicellulose, and lignin (Beall, 1969).

Stepwise regression analyses revealed that final carbonization temperature (Table 2) was the only variable that significantly reduced total variation in char yield relative to the other variables (species, particle size, and heating rate). Analysis of variance tests, however, showed that a significant difference (at the 0.05 significance level) existed among char yields from specimens of different species and particle sizes subjected to different heating rates within each final carbonization temperature. Species, particle size, and heating rate did have consistent effects on char yield (Lunden 1982), thereby accounting for the analysis of variance tests confirming statistical variation among the three variables. However, these effects were insignificant when compared with the effect of final carbonization temperature on char yield.

In a large-scale wood carbonizing system variation in particle size, heating rate, and temperature gradients would be inevitable. The present study has shown that except for maximum carbonization temperature, char yield would be relatively insensitive to these gradients within the constraints of the parameters investigated. Different species could also be carbonized with a fairly consistent char yield.

Elemental analysis of carbonized wood

Carbon content values as a percentage of oven-dry weight of carbonized and noncarbonized (control) specimens are tabulated in Table 3. Elemental carbon

TABLE 3. *Average carbon content values (percent of oven-dry weight) as a function of final carbonization temperature.*

Surface area to volume ratio	Heating rate (C/min)	Carbon content (percent oven-dry weight)[1]					
		Final carbonization temperature (C)			Final carbonization temperature (C)		
		250	400	600	250	400	600
		Red maple			*White oak*		
100	5	48.33	72.57	86.99	50.47	72.65	88.60
	15	48.33	73.12	87.00	—	71.98	85.85
	25	—	74.48	87.85	—	72.68	85.77
51	5	48.84	69.80	83.93	48.56	70.52	85.03
	15	—	69.25	—	49.64	—	87.11
	25	—	72.23	85.89	48.50	—	86.09
12	5	48.39	73.09	86.53	50.26	73.76	88.48
	15	—	73.75	86.88	—	72.39	—
	25	48.71	74.30	—	—	—	—
8	5	48.96	73.49	84.54	49.87	71.91	89.81
	15	—	73.67	84.83	—	71.48	88.30
	25	—	70.02	83.96	—	71.32	—
		Longleaf pine			*Hybrid poplar*		
100	5	50.21	74.31	89.16	50.50	75.57	89.28
	15	—	73.34	85.85	—	72.81	86.44
	25	—	74.70	86.15	—	74.11	84.24
51	5	49.34	71.60	87.30	48.76	71.84	85.65
	15	50.73	—	—	—	—	—
	25	49.69	—	—	—	—	—
12	5	50.41	76.06	87.70	48.67	74.78	85.90
	15	—	72.86	—	49.87	—	—
	25	—	73.77	—	50.45	—	—
8	5	50.03	73.25	86.53	48.56	73.17	86.44
	15	—	73.10	85.53	—	74.24	86.29
	25	—	73.26	84.38	—	75.68	85.00

[1] Noncarbonized control values: 1) red maple—45.88%, 2) white oak—47.53%, 3) longleaf pine—48.80%, and 4) hybrid poplar—47.75%.

content increases exponentially with increasing carbonization temperature. Carbon content is lowest in noncarbonized specimens, increases slightly in specimens pyrolyzed to 250 C, and comprises a substantial proportion of the oven-dry weight of specimens heated to 400 C and 600 C. Average carbon content averaged over all species, sizes, and heating rates increases by about 33% from 250 C to 400 C and about 15% from 400 C to 600 C. The carbon content values in Table 3 are slightly lower than the values given in Wenzl (1970).

Average hydrogen content (Table 4) decreases with increasing carbonization temperature. As is the case with carbon content, there is little difference between control and 250 C specimens, which is expected since little mass loss occurs in specimens pyrolyzed to 250 C. The hydrogen content values in Table 4 are similar to values reported by Wenzl (1970).

The hydrogen to carbon ratio (Table 5) is expressed on a volume basis and relates to completeness of burn, and in particular soot and smoke formation. Generally, the lower the hydrogen to carbon ratio, the greater the potential for soot and smoke formation upon combustion of the fuel. The average hydrogen

TABLE 4. *Average hydrogen content values (percent of oven-dry weight) as a function of final carbonization temperature.*

Surface area to volume ratio	Heating rate (C/min)	Hydrogen content (percent oven-dry weight)[1]					
		Final carbonization temperature (C)			Final carbonization temperature (C)		
		250	400	600	250	400	600
		Red maple			*White oak*		
100	5	5.97	3.82	2.40	5.77	3.56	2.36
	15	5.87	3.79	2.41	—	3.71	2.49
	25	—	3.68	2.31	—	3.61	2.47
51	5	5.91	3.91	2.38	5.89	3.80	2.40
	15	—	3.91	—	5.86	—	2.47
	25	—	3.78	2.30	5.93	—	2.49
12	5	5.93	3.72	2.36	5.86	3.72	2.56
	15	—	3.77	2.57	—	3.69	—
	25	6.02	3.68	—	—	—	—
8	5	5.89	3.65	2.61	5.87	3.81	2.35
	15	—	3.73	2.62	—	4.03	2.50
	25	—	4.11	2.61	—	3.79	2.50
		Longleaf pine			*Hybrid poplar*		
100	5	6.14	4.32	2.87	6.06	3.87	2.57
	15	—	4.29	2.74	—	3.91	2.66
	25	—	4.23	2.70	—	3.82	2.68
51	5	5.93	4.47	2.60	6.02	4.07	2.67
	15	6.05	—	—	—	—	—
	25	6.22	—	—	—	—	—
12	5	6.13	4.43	2.72	5.96	3.67	2.56
	15	—	4.34	—	5.89	—	—
	25	—	4.43	—	5.90	—	—
8	5	6.08	4.30	2.75	5.91	3.88	2.62
	15	—	4.34	2.85	—	4.13	2.63
	25	—	4.58	2.80	—	3.65	2.59

[1] Noncarbonized control values; 1) red maple—5.94%, 2) white oak—5.94%, 3) longleaf pine—6.22%, and 4) hybrid poplar—6.11%.

to carbon ratio values in Table 5 decrease with increasing carbonization temperature.

Mean carbon and hydrogen contents and hydrogen to carbon ratios of noncarbonized and carbonized specimens were used to develop regression equations. As with char yield, variability in hydrogen and carbon contents were primarily due to final carbonization temperature (Table 2).

Carbon and hydrogen contents were relatively consistent within each temperature range, and no particle size, heating rate, or species trends were readily apparent. Nitrogen values for the char were recorded but not analyzed because the specimens were carbonized in a nitrogen atmosphere, and it was impossible to segregate the nitrogen content into proportions inherent in the char and/or adsorbed from the carrier gas.

Higher heating values of carbonized wood

Mean higher heating values (gross heat of combustion) in Table 6 of control and pyrolyzed wood specimens (oven-dry basis) were statistically analyzed for

TABLE 5.　*Average hydrogen to carbon ratios (volume basis) as a function of final carbonization temperature.*

Surface area to volume ratio	Heating rate (C/min)	Hydrogen to carbon ratios (volume basis)[1]					
		Final carbonization temperature (C)			Final carbonization temperature (C)		
		250	400	600	250	400	600
		---------------- Red maple ----------------			---------------- White oak ----------------		
100	5	1.48	0.63	0.33	1.37	0.59	0.32
	15	1.46	0.62	0.33	—	0.62	0.35
	25	—	0.59	0.32	—	0.60	0.35
51	5	1.45	0.67	0.34	1.46	0.65	0.34
	15	—	0.68	—	1.42	—	0.34
	25	—	0.63	0.32	1.47	—	0.35
12	5	1.47	0.61	0.33	1.40	0.61	0.35
	15	—	0.61	0.36	—	0.61	—
	25	1.48	0.59	—	—	—	—
8	5	1.44	0.60	0.37	1.42	0.64	0.31
	15	—	0.61	0.37	—	0.68	0.34
	25	—	0.70	0.37	—	0.64	—
		---------------- Longleaf pine ----------------			---------------- Hybrid poplar ----------------		
100	5	1.47	0.70	0.39	1.44	0.61	0.35
	15	—	0.70	0.38	—	0.64	0.37
	25	—	0.68	0.38	—	0.62	0.38
51	5	1.44	0.75	0.36	1.48	0.68	0.37
	15	1.43	—	—	—	—	—
	25	1.50	—	—	—	—	—
12	5	1.46	0.70	0.37	1.47	0.59	0.36
	15	—	0.71	—	1.42	—	—
	25	—	0.72	—	1.40	—	—
8	5	1.46	0.70	0.38	1.46	0.64	0.36
	15	—	0.71	0.40	—	0.67	0.37
	25	—	0.75	0.40	—	0.58	0.37

[1] Noncarbonized control values: 1) red maple—1.55, 2) white oak—1.50, 3) longleaf pine—1.53, and 4) hybrid poplar—1.54.

significant differences and regression equations were developed. Averaging over all species, heating rates, and particle sizes, gross heat of combustion values increased slightly from control to 250 C specimens, by almost 33% from 250 C to 400 C, and by 15% from 400 C to 600 C. It is interesting to note that the magnitude of these increases was nearly identical to the magnitude of the increase in carbon content with increasing carbonization temperature. Also, while percent carbon and gross heat of combustion values increased by 33% from 250 C to 400 C specimens, about 66% of the dry weight was lost in this temperature range. Similarly, while percent carbon and gross heat of combustion values increased by about 15% from 400 C to 600 C specimens, almost 25% of the dry weight was lost in this temperature range.

Stepwise regression analysis was used to evaluate gross heat of combustion data (Table 6). The full model tested was gross heat of combustion, the dependent variable, as a function of carbon content, hydrogen content, and final carbonization temperature. The only variable that significantly reduced total variation in the dependent variable was carbon content.

TABLE 6. *Average higher heating values (cal/g) as a function of final carbonization temperature.*

Surface area to volume ratio	Heating rate (C/min)	Higher heating values (cal/g)[1]					
		Final carbonization temperature (C)			Final carbonization temperature (C)		
		250	400	600	250	400	600
		Red maple			*White oak*		
100	5	4,572	6,783	7,794	4,786	6,600	7,949
	15	4,574	6,725	7,795	4,756	6,520	7,878
	25	4,594	6,796	7,879	4,759	6,597	7,454
51	5	4,782	6,540	7,800	4,771	6,331	7,894
	15	4,689	6,732	7,817	4,848	6,296	7,791
	25	4,689	6,681	7,735	4,803	7,223	7,855
12	5	4,742	6,698	7,829	4,861	6,714	7,957
	15	4,711	6,872	7,883	4,840	6,609	7,897
	25	4,752	6,575	7,929	4,806	6,651	7,846
8	5	4,798	6,895	7,898	4,768	6,642	7,983
	15	4,744	6,946	7,871	4,738	6,516	7,918
	25	4,771	6,773	7,852	4,857	6,672	7,887
		Longleaf pine			*Hybrid poplar*		
100	5	4,836	6,798	7,954	4,694	6,845	7,895
	15	4,845	6,803	7,894	4,713	6,902	7,842
	25	4,864	6,825	7,830	4,680	6,892	7,718
51	5	4,907	6,903	7,968	4,719	6,677	7,850
	15	4,903	7,297	8,007	4,721	6,687	7,822
	25	4,839	7,114	7,999	4,661	6,717	7,832
12	5	5,002	6,997	7,954	4,730	6,957	7,922
	15	4,941	6,943	7,933	4,799	6,952	7,648
	25	4,874	6,934	7,867	4,856	6,842	7,873
8	5	4,898	7,023	8,003	4,750	7,005	7,969
	15	4,912	7,007	7,849	4,776	6,811	7,868
	25	4,928	7,037	7,667	4,709	6,868	7,653

[1] Noncarbonized control values: 1) red maple—4,611 cal/g, 2) white oak—4,632 cal/g, 3) longleaf pine—4,748 cal/g, and 4) hybrid poplar—4,653 cal/g.

From Table 2 it is evident that a linear relationship exists between gross heat of combustion and carbon content of fuel. This confirms the findings of Susott et al. (1975). Statistical analyses have shown that gross heat of combustion varies as a function of specimen carbon content, which in turn varies as a function of final carbonization temperature.

Dulong's formula

Dulong's formula (Babcock and Wilcox 1975), Eq. (1), is a means of theoretically calculating the higher heating value of a fuel (usually coal) whose carbon, hydrogen, oxygen, and sulfur contents are known.

$$HHV = 8,080C + 34,460(H_2 - O_2/8) + 2,205S \qquad (1)$$

where

HHV = higher heating value (cal/g),
C = fractional carbon content (dry weight basis),

H_2 = fractional hydrogen content (dry weight basis),
O_2 = fractional oxygen content (dry weight basis), and
S = fractional sulfur content (dry weight basis).

Coefficients in Eq. (1) are the known heating values of carbon (as graphite—8,080 cal/g), hydrogen (34,460 cal/g), and sulfur (2,250 cal/g).

The negative term in Dulong's formula accounts for oxidized hydrogen in the fuel. It is assumed that all hydrogen bonded to oxygen is in the form of water, i.e., these hydrogen atoms are completely oxidized and therefore cannot generate heat energy when the fuel is burned during gross heat of combustion determinations. The proportion of oxygen in the fuel bonded to hydrogen is described as $O_2 \times \dfrac{4}{16}$, where O_2 is the fractional oxygen content (dry weight basis), 16 is the atomic weight of oxygen, and 2 is the valence of one atom of oxygen in water.

In order to apply Dulong's formula to data generated in the current study, oxygen and ash contents had to be calculated. It was assumed that wood and char specimens were only composed of nitrogen, carbon, hydrogen, oxygen, and ash. Ash contents of red maple, white oak, longleaf pine, and hybrid poplar were assumed to be 0.7%, 0.4%, 0.4%, and 0.5% dry weight basis, respectively (Slocum et al. 1978; Panshin and de Zeeuw 1970; Koch 1972; Bowersox et al. 1979). Ash content of char was calculated by

$$Ash = (1/Ch \times A) \times 100 \qquad (2)$$

where

Ash = percent ash content of char, dry weight basis,
Ch = fractional char yield, dry weight basis, and
A = fractional ash content of wood, dry weight basis.

Oxygen content of the specimens was then calculated by subtraction.

Calculated oxygen values along with measured carbon and hydrogen values were used in Dulong's formula (Eq. 1). While calculated higher heating values using Dulong's formula were within ±5 percentage points of actual values of 600 C specimens, the difference between calculated and actual values grew progressively greater with specimens carbonized at lower temperatures. That is, Dulong's formula became a poorer predictor of heating values as oxygen content of the fuel increased. Therefore, it was necessary to modify Dulong's formula to account for this discrepancy.

It is believed that the discrepancy between predicted and actual values is associated with Dulong's assumption that only hydrogen exists in an oxidized state in the fuel, not carbon. Thus it was theorized that Dulong's assumption was not correct for the specimens in the current study, i.e., that some proportion of oxygen in the fuel was also bonded to carbon atoms such that a partial amount of carbon as well as hydrogen would not generate the maximum heat energy in gross heat of combustion determinations. Therefore, it was necessary to determine the proportional amounts of oxygen combining with carbon and hydrogen.

A maximum higher heating value for wood or char was defined as the value resulting from heat generated by all carbon and hydrogen in the fuel:

$$HHV_{max} = C \ (8,080 \ cal/g) + H_2 \ (34,460 \ cal/g) \qquad (3)$$

where

HHV_{max} = theoretical maximum heating value of fuel (cal/g),
H_2 = hydrogen content (fractional dry weight), and
C = carbon content (fractional dry weight).

The difference between HHV_{max} and HHV (actual higher heating value measured through calorimetry) was assumed to be the unknown amount of oxygen combining with carbon to form carbon dioxide, and an unknown amount of oxygen combining with hydrogen to form water. That is,

$$\Delta HHV = HHV_{max} - HHV \qquad (4)$$

and

$$\Delta HHV = 8{,}080(O_2/4 \times O_c) + 34{,}460(O_2/8 \times O_h) \qquad (5)$$

where

ΔHHV = cal/g,
O_c = fractional oxygen content combining with carbon to form carbon dioxide, and
O_h = fractional oxygen content combining with hydrogen to form water.

The amount of oxygen bonded to hydrogen, e.g., to form water is $O_2/8$. The amount of O_2 bonded to carbon as carbon dioxide is described by $O_2 \times \dfrac{4}{16}$, where 16 is the atomic weight of oxygen and 4 is the valence of two atoms of oxygen in carbon dioxide.

O_h and O_c were further defined by

$$O_H(O_2) + O_c(O_2) = O_2$$

or

$$O_c = 1 - O_h \qquad (6)$$

since the amount of oxygen bonded to hydrogen and the amount of oxygen bonded to carbon must equal the total amount of oxygen present in the fuel.

Solving for O_h by substituting Eq. (6) into Eq. (5) gives

$$\Delta HHV = 8{,}080[(O_2/4)(1 - O_h)] + 34{,}460(O_2/8 \times O_h) \qquad (7)$$

and rearranging,

$$O_h = \Delta HHV - (2{,}020 \times O_2)/(2{,}287.5 \times O_2). \qquad (8)$$

If the value calculated for O_h was negative, O_h was assumed to equal zero. Equation (6) was used to solve for O_c.

The final form of the modified Dulong's formula accounting for combination of oxygen with carbon as well as with hydrogen was

$$HHV_T = 8{,}080(C) - 8{,}080(O_2/4 \times O_c) + 34{,}460(H_2)$$
$$- 34{,}460(O_2/8 \times O_h) \qquad (9)$$

where

HHV_T = theoretical higher heating value of fuel (cal/g).

Theoretical higher heating values were then generated using data from the current study (Lunden 1982). An indication of the relationship between the measured values and calculated values was evaluated by

$$\% \text{ Difference} = \frac{HHV_T - HHV}{HHV_T} \times 100. \tag{10}$$

Of 212 observations mean percent difference was 1.02% with 121 observations having 0% difference, 66 observations having 0.3% difference, and 25 observations having 3–6.5% difference. There were no differences between calculated and actual gross heat of combustion values for controls and specimens carbonized to 250 C. No trend was apparent in the percent difference between calculated and actual gross heat of combustion values for 400 C and 600 C specimens.

Two factors were primarily responsible for discrepancies between calculated and measured values. Oxygen content of the specimens was calculated theoretically rather than measured. Second, it was assumed that all oxygen bonded to hydrogen was in the form of water and that all oxygen bonded to carbon was in the form of carbon dioxide, so none of these carbon and hydrogen atoms were counted as contributing to heat energy generated in gross heat of combustion determinations. However, some oxygen was probably bonded to carbon as carbon monoxide and to hydrogen as hydroxide ions, and these carbon and hydrogen atoms would generate some heat energy upon oxidation of the fuel.

SUMMARY

Char yield from wood carbonized in a flowing nitrogen atmosphere varied with final carbonization temperature. Char yield was relatively insensitive to the parameters of particle size and heating rate. Red maple, white oak, hybrid poplar, and longleaf pine yielded similar amounts of char under the conditions tested and it appears that these species could be carbonized with a fairly consistent char yield.

Carbon and hydrogen contents of char varied primarily as a function of final carbonization temperature. A linear relationship was found between gross heat of combustion and carbon content of wood and char specimens.

Dulong's formula, a means of theoretically calculating gross heat of combustion values of coals, was modified to suit wood and wood char. The basis of the modification was the assumption that some carbon as well as hydrogen is already oxidized as carbon dioxide and water in the wood and char prior to the gross heat of combustion tests.

REFERENCES

BABCOCK, G. H., AND S. WILCOX. 1975. Steam—its generation and use. The Babcock and Wilcox Co., NY. pp. 6-5-6-6.

BAILEYS, R. T., AND P. R. BLANKENHORN. 1982. Calorific and porosity development in carbonized wood. Wood Sci. 15(1):19–27.

BEALL, F. C. 1969. Thermogravimetric analysis of wood lignin and hemicelluloses. Wood Fiber 1(3): 215–226.

———, P. R. BLANKENHORN, AND G. R. MOORE. 1974. Carbonized wood—physical properties and use as an SEM preparation. Wood Sci. 6(3):212–219.

BLANKENHORN, P. R., G. M. JENKINS, AND D. E. KLINE. 1972. Dynamic mechanical properties and microstructure of some carbonized hardwoods. Wood Fiber 4(3):212–224.

————, D. P. BARNES, D. E. KLINE, AND W. K. MURPHEY. 1978. Porosity and pore size distribution of black cherry carbonized in an inert atmosphere. Wood Sci. 11(1):23–29.

BOWERSOX, T. W., P. R. BLANKENHORN, AND W. K. MURPHEY. 1979. Heat of combustion, ash content, nutrient content, and chemical content of *Populus* hybrids. Wood Sci. 11(4):257–261.

CHEREMISINOFF, P. N., AND A. C. MORRESI. 1976. Energy from solid wastes. Marcel Dekker, Inc., New York, pp. 363–366.

DEMETER, J. J., C. R. McCANN, J. M. EKMANN, AND D. BIENSTOCK. 1977. Combustion of char from pyrolyzed wood waste. NTIS Energy Research Abstracts, ABS. No. 54088, Pittsburgh Energy Research Center, pp. 1–25.

HAMMOND, V. L., L. K. MUDGE ET AL. 1974. Energy from forest residuals by gasification of wood wastes. Pulp Paper 48(2):54–57.

KANURY, A. M. 1972. Thermal decomposition kinetics of wood pyrolysis. Combustion Flame 18: 75–83.

KNIGHT, J. A., AND M. D. BOWEN. 1975. Pyrolysis—a method for conversion of forestry wastes to useful fuels. Southeast Tech. Div. of American Pulpwood Association, Fall Meeting.

KOCH, P. 1972. Utilization of the southern pines, vol. I. USDA For. Serv., So. For. Exp. Sta., Agric. Handbook No. 420, pp. 188–226.

LEWELLEN, P. C., W. A. PETERS, AND J. B. HOWARD. 1976. Celoulose pyrolysis kinetics and char formation mechanism. 16th symposium on combustion. Fire Expl. Res. 1471–1480.

LUNDEN, G. W. 1982. Selected properties and char yield of wood carbonized in a nitrogen atmosphere. M.S. thesis, The Pennsylvania State University. 70 pp.

McGINNES, E. A., JR., S. A. KANDEEL, AND P. S. SZOPA. 1971. Some structural changes observed in the transformation of wood into charcoal. Wood Fiber 3(2):77–83.

MILNE, T. 1979. Pyrolysis—the thermal behavior of biomass below 600°C. *In* Vol. II—Principles of gasification. Solar Energy Research Institute, CO. Pp. 97–122.

MOORE, G. R., P. R. BLANKENHORN, F. C. BEALL, AND D. E. KLINE. 1974. Some physical properties of birch carbonized in a nitrogen atmosphere. Wood Fiber 6(3):193–199.

PANSHIN, A. J., AND C. DE ZEEUW. 1970. Textbook of wood technology. McGraw-Hill Book Company, New York. 705 pp.

REED, T. B., AND D. JANTZEN. 1979. A survey of biomass gasification. *In* Vol. II—Principles of gasification. Solar Energy Research Institute, CO. I23–I17.

ROBERTS, A. F. 1970. A review of kinetics data for the pyrolysis of wood and related substances. Combustion Flame 14:261–371.

SHAFIZADEH, F. 1968. Pyrolysis and combustion of cellulosic materials. Adv. Carbohydrate Chem. 23:419.

————. 1980. Introduction to pyrolysis of biomass. Specialists' Workshop on Flash Pyrolysis of Biomass Proceedings, Solar Energy Res. Institute of DOE, CO. Pp. 79–101.

SLOCUM, D. H., E. A. McGINNES, JR., AND F. C. BEALL. 1978. Charcoal yield, shrinkage, and density changes during carbonization of oak and hickory woods. Wood Sci. 11(1):42–47.

SUSOTT, R. A. 1980. Effect of heating rate on char yield from forest fuels. USDA For. Serv. Res. Note, INT-295, Intermountain For. and Range Exp. Sta., Utah, pp. 1–6.

————, W. F. DEGROOT, AND F. SHAFIZADEH. 1975. Heat content of natural fuels. J. Fire Flamm. 6:311–325.

WENZL, H. F. J. 1970. The chemical technology of wood. Chapter 2. Academic Press, New York. Pp. 260–300.